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(54) [Title of the Invention]

POLYCARBONATE-BASED RESIN COMPOSITION**[Claims]**

[Claim 1] A polycarbonate-based resin composition comprising 10 to 90% by weight polycarbonate-polyorganosiloxane copolymer, 10 to 60% by weight glass fibers and 0 to 80% by weight polycarbonate resin, and the amount of the polyorganosiloxane is 0.5 to 40% by weight of the resin components.

[Detailed Description]**[Industrial Field of the Invention]**

The present invention relates to a polycarbonate-based resin composition and, more specifically to a glass fiber-reinforced polycarbonate-based resin composition with especially good impact resistance and suitability for use in various industrial materials.

[Prior Art and Statement of the Problem]

Polycarbonate resins have excellent mechanical strength, electrical properties, transparency, etc., and have been used in a variety of fields as engineering plastics.

Glass fiber-reinforced polycarbonate resins are well known in which glass fibers are incorporated into these kinds of polycarbonate resins to improve their rigidity and dimensional stability.

However, the addition of glass fibers causes a drop in Izod impact strength due to brittle fracture.

Therefore, compositions have been proposed that include organopolysiloxane in addition to glass fiber-reinforced polycarbonate resin (see Japanese Patent (Koho) Publication No. 59-35929 and Japanese Patent (Kokai) Publication No. 57-501860).

Still, a problem with molded articles obtained from such compositions is that they have poor insulating properties.

With that problem in mind, compositions of glass fiber-reinforced polycarbonate resins containing a small amount of organopolysiloxane/polycarbonate copolymers have been proposed (see Japanese Patent (Kokai) Publication No. 55-160052).

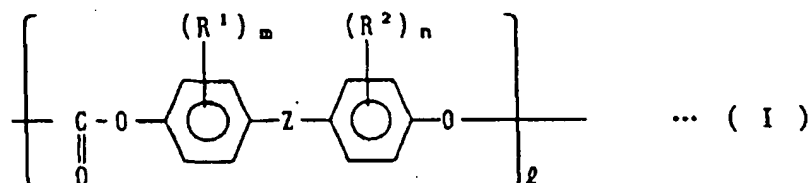
While such compositions are improved in terms of impact resistance to some extent, such improvement is not large, and their impact resistance is still not good enough for use in fields in which especially high impact resistance is needed such as chassis or electrically powered tools and the like.

[Solution to the Problem]

As a result of extensive investigation to provide a solution to the above problems, it has been found that a polycarbonate-based resin composition with superior impact resistance, rigidity, dimensional stability, and the like can be obtained by using a polycarbonate-polyorganosiloxane copolymer, glass fibers and a

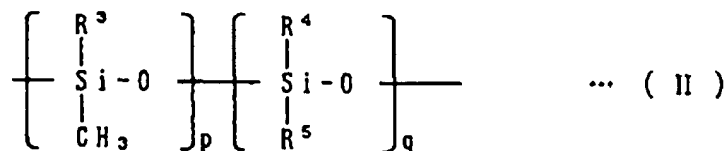
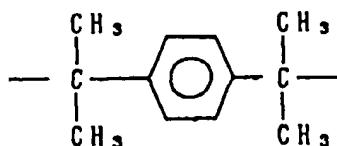
polycarbonate resin mixed in a specific proportion, and such findings provide the basis for the present invention. More specifically, the present invention provides a polycarbonate-based resin composition, characterized by comprising 10 to 90% by weight polycarbonate-polyorganosiloxane copolymer, 10 to 60% by weight glass fibers and 0 to 80% by weight polycarbonate resin, and the amount of polyorganosiloxane is 0.5 to 40% by weight of the resin components.

The polycarbonate-polyorganosiloxane copolymer used in the present invention is comprised of a polycarbonate segment having repeating units expressed by the following formula I



(wherein: Z is single bond, ether bond, alkylene group having 1 to 8 carbon atoms, an alkylidene group having 2 to 8 carbon atoms, a cycloalkylene group having 5 to 15 carbon atoms, a cycloalkylidene group having 5 to 15 carbon atoms, a sulfonyl

group, a sulfoxide group, a carbonyl group, sulfide group, or a group represented by the following general formula; R¹ and R², each represents a hydrogen atom, a halogen atom or an alkyl group having 1 to 8 carbon atoms and may be identical or different; m and n each represents an integer of 1 to 4, provided that when m is 2 or more, R¹ may be identical or different and when n is 2 or more, R² may be identical or different, and l [Tr. omitted but inferred from context] is between 3 and 50), and a polyorganosiloxane segment having repeating units expressed by the following general formula



(wherein R³, R⁴ and R⁵ each represents a hydrogen atom, an alkyl group having 1 to 6 carbon atoms or a phenyl group and may be identical or different, and p and q each represents an integer of 1 or more.)

Usually, the polyorganosiloxane segment has a degree of polymerization of 5 to 300.

The above polycarbonate-polyorganosiloxane copolymer is a block copolymer comprising the polycarbonate segment having repeating units expressed by General Formula (I) and the polyorganosiloxane segment having repeating units expressed by General Formula (II), and it has a viscosity-average molecular weight of 10,000 to 40,000, preferably 15,000 to 35,000.

This kind of polycarbonate-polyorganosiloxane copolymer may be prepared, for example, by dissolving a pre-prepared polycarbonate oligomer forming the polycarbonate segment and a polyorganosiloxane having a terminal reactive group and forming the polyorganosiloxane segment in a solvent such as methylene chloride, chlorobenzene or pyridine, adding an

aqueous sodium hydroxide solution containing bisphenol, and subjecting that solution to an interface reaction with a catalyst such as triethylamine or trimethyl benzylammonium chloride. Polycarbonate-polyorganosiloxane copolymers prepared by the methods presented in Japanese Patent (Koho) Publication Nos. 44-30108 and 45-20510.

The polycarbonate having repeating units represented by General Formula (I) may be prepared by a solvent method, i.e., one in which a dihydric phenol is allowed to react with a carbonate precursor such as phosgene or subjected to an ester exchange reaction with a carbonate precursor such as diphenyl carbonate in a solvent such as methylene chloride in the presence of a publicly known acid acceptor and a molecular-weight regulator.

The most suitable dihydric phenols to be used in the present invention include bisphenols, and 2,2-bis(4-hydroxyphenyl) propane (bisphenol A) is preferred. The bisphenol A may be partly or wholly substituted by other dihydric phenols. Dihydric

phenols other than bisphenol A include compounds such as (4-hydroxyphenyl) alkanes other than bisphenol A, hydroquinone, 4,4' dihydroxydiphenyls, bis(4-hydroxyphenyl) cycloalkanes, bis(4-hydroxyphenyl) sulfides, bis(4-hydroxyphenyl) sulfones, bis(4-hydroxyphenyl) sulfoxides, bis(4-hydroxyphenyl) ethers and bis(4-hydroxyphenyl) ketones or halogenated bisphenols such as bis(3,5-dibromo-4-hydroxyphenyl) propane and bis (3,5-dichloro-4-hydroxyphenyl) propane.

The polycarbonate may be a homopolymer (oligomer) of one of these dihydric phenols or a copolymer containing two or more thereof; alternatively, it may be a thermoplastic randomly branched polycarbonate obtained by using the above dihydric phenols in combination with a polyfunctional aromatic compound.

The polyorganosiloxane represented by General Formula (II) may be obtained, for example, by the reaction of a dialkyl dichlorosilane and/or diaryl dichlorosilane with water. Monomers of such a polyorganosiloxane include dimethylsiloxane or methylphenylsiloxane.

The kind of polycarbonate-polyorganosiloxane copolymer described above is incorporated into the composition at a proportion of 10 to 90% by weight, preferably 15 to 80% by weight. If the amount of this copolymer is less than 6% by weight, there is then no improvement in impact resistance. If the amount is higher than 90% by weight, on the other hand, there is a decrease in dimensional stability.

The amount of organosiloxane contained in the resin other than the glass component (the total amount of polycarbonate-polyorganosiloxane copolymer and polycarbonate resin) is 0.5 to 40% by weight, preferably 1.0 to 35% by weight. If the amount of the organosiloxane is less than 0.5% by weight, there is no improvement in impact resistance. If the amount exceeds 40% by weight, on the other hand, a copolymer having sufficient molecular weight cannot be obtained.

Glass fibers are also used in the present invention. Any alkali-containing glass, low-alkali glass or non-alkali glass may be used therein. Preferably, the glass fibers used are 1 to 8 mm long, preferably 3 to 6 mm long, and 3 to 20 μ m, preferably 5 to 15 μ m in diameter. The glass fibers may be used in any nonrestrictive forms such as roving, milled fibers and chopped strands, and may be used alone or in combinations of two or more types.

Glass fibers that have been surface-treated with silane coupling agents such as aminosilanes, epoxysilanes, vinylsilanes or methacrylsilanes, or chromium complex compounds, boron compounds or like other compounds may be used to improve their affinity with respect to the polycarbonate-polyorganosiloxane copolymers and polycarbonate resins.

The kinds of glass fibers described above are incorporated into the composition at a proportion of 10 to 60% by weight, preferably 15 to 55% by weight. If the proportion of the glass

fibers is less than 10% by weight, it causes an undesirable decrease in dimensional stability. If the proportion of the glass fibers exceeds 60% by weight, kneading becomes impossible, which is also undesirable.

Furthermore, a polycarbonate resin may be used in the present invention, if needed.

The polycarbonate resin has repeating units represented by General Formula (I) and, as mentioned above, may be easily obtained by the reaction of a dihydric phenol with phosgene, for example. These dihydric phenols include such phenols mentioned above.

From the standpoint of mechanical strength and molding properties, the polycarbonate resin used in the present invention preferably has a viscosity-average molecular weight of 10,000 to 100,000, and optimally 20,000 to 40,000.

This polycarbonate resin is incorporated into the composition at a proportion of 0 to 80% by weight, preferably 0 to 70% by weight. If the proportion of the polycarbonate resin exceeds 80% by weight, there is no improvement in impact resistance.

The inventive polycarbonate-based resin composition is comprised of the above polycarbonate-polyorganosiloxane copolymer, glass fibers and polycarbonate resin, and may additionally contain various additives, as needed, provided that the object of the present invention is still achieved. For example, carbon fibers, metal fibers, inorganic fillers, metal powders, UV absorbers, flame retardants, colorants, and the like may be added.

The inventive polycarbonate-based resin composition may be obtained by blending and kneading the above components together. For this purpose, blending and kneading may be carried out in a conventional manner using, for example, ribbon blenders, Henschel mixers, Banbury mixers, drum tumblers, single-, twin- or multi-screw extruders, co-kneaders or like other equipment. For kneading, a heating temperature of 250 to 300°C is usually suitable.

[Examples]

The present invention will now be explained in greater detail with reference to the following examples.

Preparation Example 1-1 (Preparation of Reactive Polydimethylsiloxane)

Over a 2 hour period, a mixture of 100 g of water and 206 g of dioxane was added to 800 g of dimethyl dichlorosilane. The resulting mixture was heated and gently refluxed with stirring until it was homogeneous. The mixture was then stripped under vacuum and adjusted to 202°C and a pressure 12 mmHg. Then, the stripped product was filtered to obtain a transparent oily product. A quantity of 225 g of this oily product was dissolved in 130 g of dried dichloromethane, and this solution was added to a mixture of 114 g of bisphenol A, 130 g of dried pyridine and 1300 g of dichloromethane. The addition took place over 65 min with intense stirring. The product was then alkali-washed using

1000 g of an aqueous solution of sodium hydroxide (0.01N), then acid-washed with 1000 g of hydrochloric acid (0.1N) and finally washed with 1000 g of water. The dichloromethane was removed by evaporation to obtain the terminal-reactive polydimethylsiloxane (hereinafter, reactive PDMS) having a terminal phenolic hydroxyl group.

Preparation Example 1-2 (Preparation of Reactive PDMS)

Reactive PDMS was obtained using the same process as described in Preparation Example 1-1 except the amount of water initially mentioned was changed from 100 g to 140 g.

Preparation Example 1-3 (Preparation of Reactive PDMS)

Silicone oil that is reactive at both terminals (KF 6002, Shinetsu Silicone Co., Ltd.) was used as the reactive PDMS.

Preparation Example 1-4 (Preparation of Reactive PDMS)

A mixture of 1483 g of octamethyl cyclotetrasiloxane, 137 g of 1,1,3,3-tetramethyl disiloxane and 35 g of 86% sulfuric acid was prepared, and the mixture was stirred at room temperature for 17 hours. The oily phase was separated, and 25 g of sodium bicarbonate was added followed by stirring for 1 hr. After filtration, the product was distilled under vacuum at 150°C and 3 mmHg to remove substances with low boiling points.

A platinum mixture was prepared by adding 294 g of the above oil at a temperature of 90°C to a mixture of 60 g of 2-allylphenol and 0.0014 g of platinum in the form of a platinum/alcolate complex. The mixture was stirred for 3 hours, while maintaining the temperature at 90°C to 115°C. The product was extracted with methylene chloride and washed three times with 80% aqueous methanol to remove excessive 2-allylphenol. The product was dried over anhydrous sodium sulfate, and the solvents were removed under vacuum at temperatures up to 115°C to obtain the reactive PDMS.

Preparation Example 1-5 (Preparation of Reactive PDMS)

Silicone oil that is reactive at both terminals (X-22-165B, Shinetsu Silicone Co., Ltd.) was used as the reactive PDMS.

Preparation Example 1-6 (Preparation of Reactive PDMS)

Silicone oil that is reactive at both terminals (X-22-165C, Shinetsu Silicone Co., Ltd.) was used as the reactive PDMS.

Preparation Example 2 (Preparation of Polycarbonate Oligomer)

A total of 60 kg of bisphenol A were dissolved in 400 [sic, probably "L" here and below] of a 5% aqueous solution of sodium hydroxide to prepare an aqueous solution of bisphenol A in sodium hydroxide. The solution was kept at room temperature. The aqueous sodium hydroxide solution of bisphenol A and methylene chloride were introduced at flow rates of 138 [L]/hr and 69 [L]/hr, respectively, into a tubular reactor 10 mm ID and m long through an orifice plate; 10.7 kg/hr phosgene was introduced concurrently, and the reaction was conducted continuously for 3 hr. The tubular reactor used had a double-walled structure designed to pass cooling water through an outer jacket to keep the discharge temperature of the reaction solution at 25°C. The discharge solution was also adjusted to pH 10-11. The aqueous phase was removed by allowing the reaction solution was allowed to stand, the methylene chloride phase (220 [L]) was collected, and 170 [L] methylene chloride was added under sufficient agitation to obtain a polycarbonate oligomer (with a concentration of 317 g/[L]). This polycarbonate oligomer (hereinafter, PC oligomer) had a degree of polymerization of 3-4.

Preparation Example 3-1 (Preparation of PC-PDMS Copolymer A)

A solution was prepared by dissolving 160 g of the reactive PDMS obtained in Preparation Example 1-1 in 2 [L] of methylene chloride, and the solution was mixed with 10 [L] of the PC oligomer obtained in Preparation Example 2. An aqueous solution of 26 g of sodium hydroxide in 1 [L] of water and 5.7 cc of triethylamine were added, followed by stirring at 500 rpm for 1 hr at room temperature. A solution of 600 g bisphenol A dissolved in 5 [L] of 5.2% by weight aqueous sodium hydroxide solution, 8 [L] methylene chloride, and 81 g p-tert-butyl phenol were added, and the mixture was stirred at 500 rpm for 2 hr at room temperature. Thereafter, an additional 5 [L] of methylene chloride were added, and a wash was performed with 5 [L] water, followed by an alkali-wash with 5 [L] of a 0.01 N aqueous sodium hydroxide solution, acid-wash with 5 [L] of 0.1 N aqueous hydrochloric acid solution, and finally a wash with 5 [L] of water in that order; finally the methylene chloride was removed to obtain a PC-PDMS copolymer A in the form of chips with a PDMS content of 3.5% by weight.

Preparation Example 3-2 (Preparation of PC-PDMS Copolymer B)

PC-PDMS copolymer B was prepared in the same manner as Preparation Example 3-1 except 500 g of the reactive PDMS obtained in Preparation Example 1-2 were used in place of 160 g of the reactive PDMS obtained in Preparation Example 1-1. The PC-PDMS copolymer B had a PDMS content of 10% by weight.

Preparation Example 3-3 (Preparation of PC-PDMS Copolymer C)

PC-PDMS copolymer C was prepared in the same manner as Preparation Example 3-1 except 2.6 kg of the reactive PDMS obtained in Preparation Example 1-2 were used in place of 160 g of the reactive PDMS obtained in Preparation Example 1-1, and the amount of sodium hydroxide used was changed from 26 g to 50 g. The PC-PDMS copolymer C had a PDMS content of 29% by weight.

Preparation Example 3-4 (Preparation of PC-PDMS Copolymer D)

A solution was prepared by dissolving 480 g of the reactive PDMS obtained in Preparation Example 1-3 (silicone oil reactive at both terminals) in 9.5 [L] of the PC oligomer obtained in Preparation Example 2, and 101 g of triethylamine was slowly added by dripping it into this solution with stirring. After the addition by dripping, the solution was stirred for 1 hr and then acid-washed with 5 [L] of 0.1 N hydrochloric acid to separate the organic phase. A solution of 600 g bisphenol A dissolved in 5 [L] of 5.2% by weight aqueous sodium hydroxide solution, 8 [L] methylene chloride, and 25 g p-tert-butyl phenol were added, and the mixture was stirred at 500 rpm for 2 hr at room temperature. Thereafter, an additional 5 [L] of methylene chloride were added, and a wash was performed with 5 [L] water, followed by an alkali-wash with 5 [L] of a 0.01 N aqueous sodium hydroxide solution, acid-wash with 5 [L] of 0.1 N aqueous hydrochloric acid solution, and finally a wash with 5 [L] of water in that order; finally the methylene chloride was removed to obtain a PC-PDMS copolymer D in the form of chips with a PDMS content of 3.9% by weight.

Preparation Example 3-5 (Preparation of PC-PDMS Copolymer E)

Macrolon Type 1207 produced by Bayer Corp., which has a PDMS content of 4.8% by weight, was used as the PC-PDMS copolymer. The PDMS content of all the above PC-PDMS copolymers was all determined by ¹H NMR.

Preparation Example 3-6 (Preparation of PC-PDMS Copolymer F)

PC-PDMS copolymer F was prepared in the same manner as in Preparation Example 3-1 except the reactive PDMS obtained in Preparation Example 1-4 was used in place of the reactive PDMS obtained in Preparation Example 1-1. The PC-PDMS copolymer F had a PDMS content of 3.5% by weight.

Preparation Example 3-7 (Preparation of PC-PDMS Copolymer G)

PC-PDMS copolymer G was prepared in the same manner as in Preparation Example 3-1 except the reactive PDMS obtained in Preparation Example 1-5 was used in place of the reactive PDMS obtained in Preparation Example 1-1. The PC-PDMS copolymer G had a PDMS content of 3.5% by weight.

Preparation Example 3-8 (Preparation of PC-PDMS Copolymer H)

PC-PDMS copolymer H was prepared in the same manner as in Preparation Example 3-1 except the reactive PDMS obtained in Preparation Example 1-6 was used in place of the reactive PDMS obtained in Preparation Example 1-1. The PC-PDMS copolymer H had a PDMS content of 3.5% by weight.

Examples 1-18 and Comparative Examples 1-5

The PC-PDMS copolymers A-H obtained in Preparation Examples 3-1 to 3-8, polycarbonate (trade name: Toughron A-2500; average molecular weight: 25,000; produced by Idemitsu Petrochemical Co., Ltd.) and glass fibers (non-alkali glass surface-treated with aminosilane; length: 6 mm; diameter: 13 μ m) were blended together at the proportions specified in Table 1, and the blends were formed into pellets through a 30-mm vented extruder; these pellets were injection-molded at a temperature of 300°C to obtain molded articles for measurement of their physical properties. The results are shown in Table 1. The glass fibers were fed into the blend downstream from the hopper through which the resin stock was fed into the extruder.

Table 1

	PC-PDMS Copolymer		Polycarbonate (% by weight)	PDMS Content of Resin Components (% by weight)	Glass fibers (%by weight)	Izod Impact Strength ^{*1} (kg·cm/cm)	Tensile Modulus ^{*2} (kg/cm ²)	Bend Strength ^{*3} (kg/cm ²)
	Type	Amount (% by weight)						
Example 1	A	50	0	3.5	50	31	84800	2400
Example 2	A	70	0	3.5	30	27	58900	1800
Example 3	A	90	0	3.5	10	20	33500	1200
Example 4	B	70	0	10	30	28	59000	1800
Example 5	C	50	0	29	50	30	85200	2300
Example 6	C	70	0	29	30	30	59000	1700
Example 7	C	90	0	29	10	21	33600	1100
Example 8	D	70	0	3.9	30	29	59100	1800
Example 9	A	30	60	1.2	10	20	33700	1200
Comparative Example 1	—	0	90	0	10	11	33700	1200
Example 10	C	10	70	3.6	20	23	46300	1600
Comparative Example 2	—	0	80	0	20	15	46500	1600
Example 11	B	20	50	2.9	30	28	59000	1800
Example 12	B	40	30	5.7	30	27	59200	1800
Example 13	B	60	10	8.6	30	27	58900	1700
Example 14	C	10	60	4.1	30	28	59000	1800
Comparative Example 3	C	5	65	2.1	30	18	58900	1700
Comparative Example 4	—	0	70	0	30	18	59000	1800
Comparative Example 5	—	0	50	0	50	19	85000	2400
Example 15	E	70	0	4.8	30	27	58900	1700
Example 16	F	70	0	3.5	30	21	58800	1700

	PC-PDMS Copolymer		Polycarbonate (% by weight)	PDMS Content of Resin Components (% by weight)	Glass fibers (%by weight)	Izod Impact Strength* ¹ (kg·cm/cm)	Tensile Modulus* ² (kg/cm ²)	Bend Strength* ³ (kg/cm ²)
	Type	Amount (% by weight)						
Example 17	G	70	0	3.5	30	22	58900	1800
Example 18	H	70	0	3.5	30	23	58800	1700

*1: Measured according to JIS-K-7110

*2: Measured according to JIS-K-7113

*3: Measured according to JIS-K-7203

[Effect of the Invention]

The polycarbonate-based resin composition according to the present invention excels in not only impact resistance but also rigidity expressed in terms of bending strength and tensile modulus of elasticity or dimensional stability.

Thus, the present compositions are effectively used in various industrial fields inclusive of electric/electronic fields, in particular fields for which high impact resistance is needed, e.g., chassis or like other fields.